

Electrochemical behaviour and electrowinning of rhodium in acidic chloride solution

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Abstract The electrochemical behaviour and recovery of rhodium in an acidic solution were investigated using a rotating disc electrode system and a modified electrochemical cyclone cell, respectively. The electrochemical polarization data indicated that the Rh^{3+} ions were reduced to metallic Rh below -0.1 V, and the limiting current density for rhodium deposition was observed at around -0.3 V (vs. SCE) with a diffusion coefficient of $6.3 \times 10^{-6} \text{ cm}^2 \text{ s}^{-1}$ using the Levich equation. The effects of the applied voltage and the initial concentration of rhodium were examined using the modified cyclone cell, and more than 91 % of the rhodium in solution was recovered within 2 h under the optimal conditions.

Keywords Rhodium · Chloride solution · Electrowinning · Cyclone cell

1 Introduction

Rhodium is one of the platinum group metals, and is a precious metal that is hard, highly reflective and very stable to oxidation. Its density is only about one half that of platinum [1]. It has mainly been used as a catalyst for automobile catalytic converters and other industrial processes, and as an alloying element for corrosion resistance [2–6]. Since rhodium is a very expensive metal, efficient

recovery from secondary sources is of considerable importance, and there has been increasing demand for the development of new extraction techniques.

Platinum group metals from automotive catalysts can be recovered by smelting the catalytic converters with Cu as a collector metal or by dissolving them in strong acid [7]. Various hydrometallurgical processes have been studied to recover platinum group metals [1, 8–10]; these processes generally involve leach liquors of low metal concentration, of around ~ 100 ppm. Several studies have been carried out on the electrodeposition of rhodium [11–14], but most of them have employed cyclic voltammetry techniques to investigate the nucleation phenomena.

To reduce the time and cost of the electrowinning process, enhancement of the mass transfer by decreasing the diffusion layer thickness is needed, particularly to recover precious metals from leach liquors of low concentration. Previously, a hydrocyclone-type electrochemical cyclone cell was employed and tested for the recovery of various metals from a dilute solution, and up to 90 % of the metal was recovered, within 6–7 h [15–17]. A similar electrochemical cyclone cell was employed, which was modified on the anode side to increase the anode area; the electrolyte could also flow through a vortex finder that served as an anode, as an alternative to the previous hydrocyclone cell, which used a graphite anode tube [18]. The cell fully utilized the principal features of the turbulent nature of the hydrodynamics in the increase hydrocyclone to increase the mass transfer rate, and more than 90 % of the precious metals was recovered within 1 h [18–20].

In this study, the electrochemical behaviour of rhodium in an acidic chloride solution was investigated using a rotating disc electrode, and electrowinning of the rhodium recovery was performed using a modified electrochemical cyclone cell.

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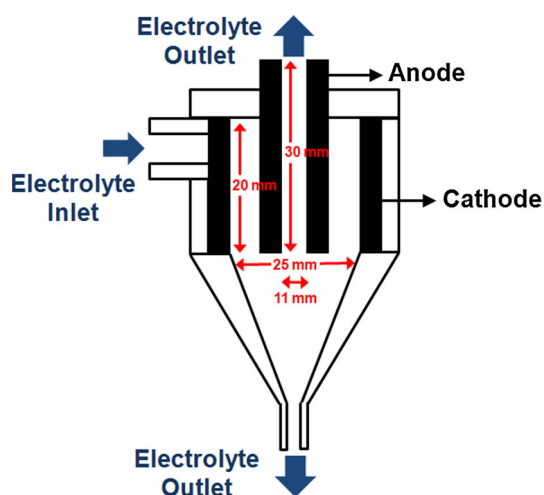


Fig. 1 Schematics of modified electrochemical cyclone cell

2 Experimental

A 0.282-cm² glassy carbon disc (Tokai Carbon) was mounted in epoxy resin and polished with 50-nm alumina powder for the rotating disc experiments. Electrolytes were prepared by dissolving RhCl₃·3H₂O (Kojima Chemicals) in distilled-deionized water, and the pH was adjusted to 2 with hydrochloric acid. A typical three-electrode system [with a glassy carbon rotating disc electrode, graphite counter electrode and saturated calomel electrode (SCE)] was employed to investigate the basic electrochemical behaviour of rhodium in the acidic solution using an EG&G model 273 potentiostat and an EG&G rotator. The cathodic polarization curves were obtained with a scan rate of 5 mV s⁻¹. All potentials are referenced to the SCE.

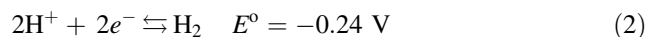
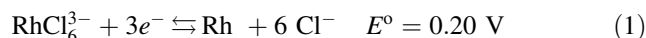
Figure 1 shows the schematics of the electrochemical cyclone reactor. A stainless steel cylinder served as the cathode, which had an inner diameter of 25 mm and a height of 20 mm. The electrolyte flowed through the apex at the bottom of the cyclone and also through the vortex finder (an anode made of a stainless-steel tube of $\phi = 11$ mm and length = 30 mm). These two electrodes were connected to a DC power supply. The tank containing the solution was coupled to an electrochemical cyclone cell by a rotary pump to control the flow rate, which was measured with a flow metre. All experiments were performed under potentiostatic conditions, and samples were periodically withdrawn, to measure the rhodium concentration by inductively coupled plasma spectroscopy (ICP-MS) (PE 5100, Perkin-Elmer).

3 Results and discussion

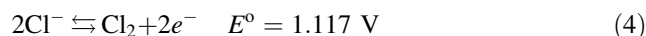
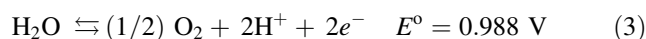
3.1 Cathodic polarization behaviours

The electrodeposition of rhodium ions in acidic chloride media can be expressed as follows [21]:

Cathode:



Anode:



where E° is the standard state potential.

Figure 2 displays the cathodic polarization curves with a variation of rotation speed at 30 °C. The open-circuit potential was close to 0.27 V, which agreed well with the value of 0.26 V, given for a chloride medium [11]. When the Rh³⁺ (RhCl₆³⁻) species started to reduce, the first plateau region appeared near 0.1 V (700 rpm case), which seemed to be related to the near-equilibrium reduction reaction between Rh³⁺ (RhCl₆³⁻) and Rh²⁺ (RhCl₅²⁻) ions. When the potential reached -0.05 V, a similar phenomenon was observed for Rh²⁺ and Rh¹⁺ (RhCl₄¹⁻) ions. As the potential decreased further, the reduction of Rh¹⁺ to metallic Rh occurred. A limiting current density region for rhodium deposition appeared at approximately -0.3 V, and hydrogen evolution reaction started at about -0.45 V.

The limiting current densities for rhodium deposition were plotted against the square root of the rotation speed, and showed good linearity, obeying the Levich equation (5) well, as shown in the inset graph in Fig. 2 [22]:

$$i_l = 0.62nFAD^{2/3}\nu^{-1/6}\omega^{1/2}C_b \quad (5)$$

Here, i_l is the limiting current density, n is the number of electrons transferred in reaction (1), F is the Faraday constant, A is the electrode area, D is the diffusivity, ν is the kinematic viscosity, ω is the electrode rotation speed

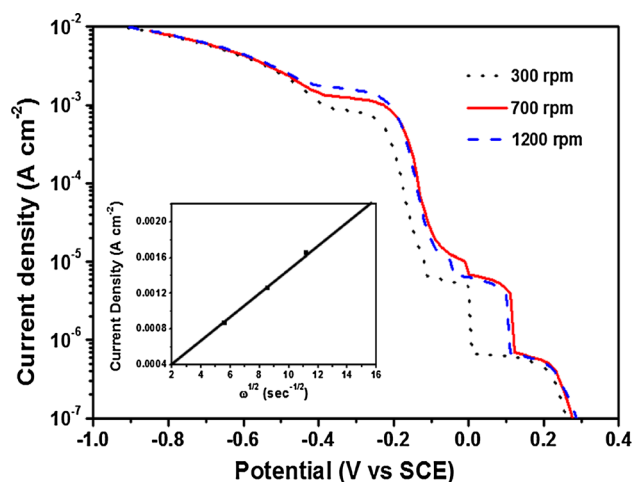


Fig. 2 Cathodic polarization curves with various rotating speeds; $C_{\text{Rh}} = 100$ ppm, pH 2, 30 °C

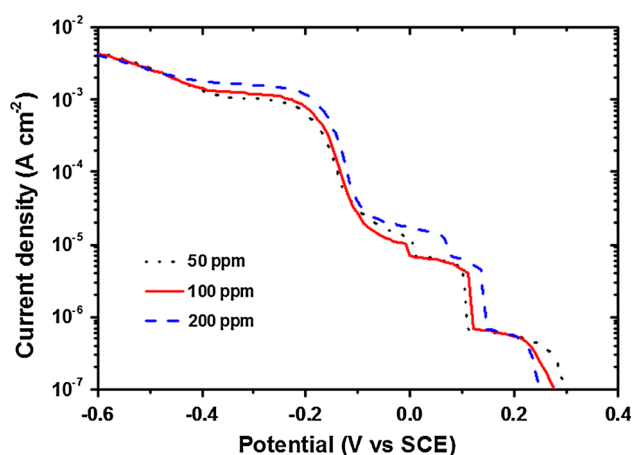


Fig. 3 Cathodic polarization curves at various concentration; pH 2, $\omega = 700$ rpm, 30°C

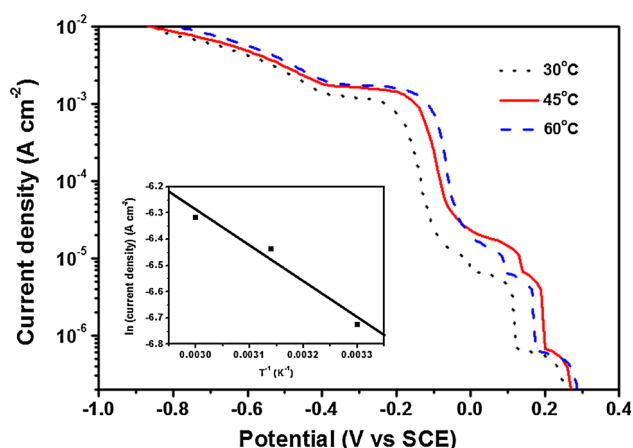


Fig. 4 Cathodic polarization curves with various solution temperature; $C_{\text{Rh}} = 100$ ppm, $\omega = 700$ rpm, pH 2

and C_b is the bulk concentration of rhodium. The diffusion coefficient of rhodium (Rh^{3+})(RhCl_6^{3-}) calculated from the slope of the inset graph in Fig. 2 was $6.3 \times 10^{-6} \text{ cm}^2 \text{ s}^{-1}$, which agreed well with the reported value. [7, 10].

The effect of rhodium concentration on cathodic polarization is shown in Fig. 3. As expected, the open-circuit potential decreased as the rhodium concentration increased, and the electrochemical behaviours were almost the same as discussed above in regard to the polarization curves.

Figure 4 illustrates the temperature dependence of the electrodeposition of rhodium. The equilibrium potential increased with temperature, according to the Nernst equation. Also, the general trends of rhodium during electrochemical reduction were similar to each other. An activation energy of $11.14 \text{ kJ mol}^{-1}$ was obtained using the Arrhenius equation, from the limiting current density.

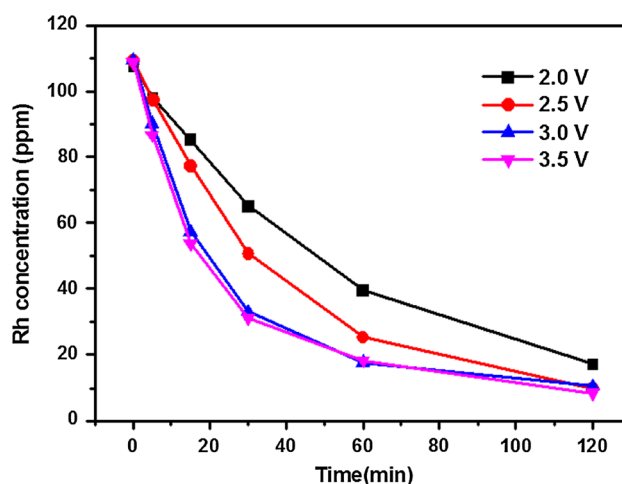


Fig. 5 Effect of applied voltage on the recovery of the rhodium; $C_{\text{Rh}} = 110$ ppm, linear solution velocity = 3.5 m s^{-1} , pH 2, ambient temperature

This indicated that a diffusional process would be the controlling step during the electrowinning of rhodium in low concentration; and the enhancement of mass transfer in the solution would be the most important factor for practical recovery of rhodium from a leach liquor of low concentration.

3.2 Electrowinning of rhodium using a modified cyclone electrochemical cell

As mentioned previously, the electrowinning of rhodium using a modified electrochemical cyclone cell was performed at ambient temperature. Figure 5 shows the effect of the applied voltage at a linear solution velocity of 3.5 m s^{-1} and pH 2. As the solution velocity increased, the recovery of rhodium increased. The optimized solution velocity was 3.5 m s^{-1} because there was no change of recovery efficiency over 3.5 m s^{-1} . The initial concentration of rhodium was 110 ppm. At 2.0 and 2.5 V, the recovery of rhodium was relatively slow with 63.2 and 76.6 % being recovered after 1 h, respectively, while the recovery reached close to 84 % at 3 and 3.5 V. Compared with the 2.5 V case, the initial rate of recovery of rhodium was much faster in the case of 3 V, while that from 3.5 V was almost the same as that at 3.0 V, which could be an optimum applied potential considering the energy consumption.

Figure 6 shows the effect of the initial concentration of rhodium on the recovery at a linear solution velocity of 3.5 m s^{-1} , pH 2 and an applied voltage of 3 V. The results indicated that the recovery rate of rhodium was slow at lower concentrations of rhodium, but for all cases, the recovery was more than 91 % within 2 h.

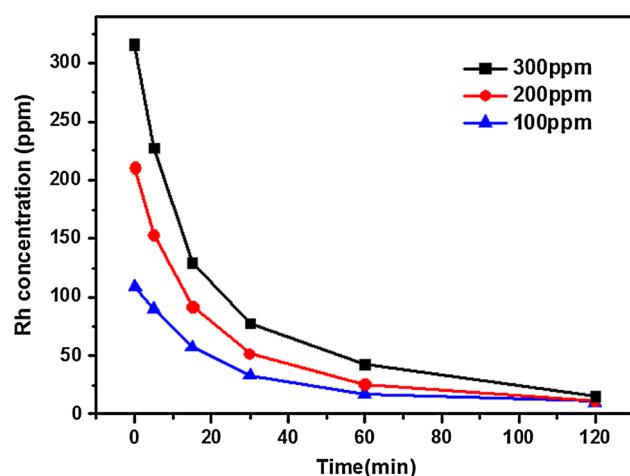


Fig. 6 Effect of initial concentration on the recovery of the rhodium; applied voltage = 3.0 V, linear solution velocity = 3.5 m s^{-1} , pH 2, ambient temperature

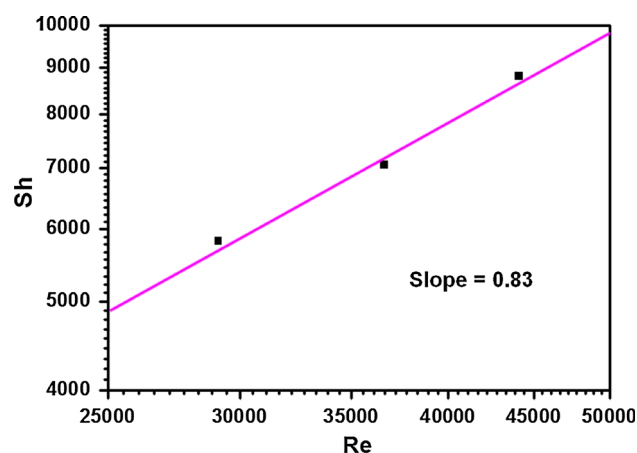


Fig. 7 Correlation of Sh and Re for the rhodium electrowinning

The effect of flow rate on the recovery of Rh was also determined. According to Lin et al. [23], when hydrodynamic conditions were turbulent flow, the mass transfer rate was in agreement with the Chilton–Colburn equation for turbulent flow [24]. Ross and Wragg [25] suggested a

modified relationship that considered cell geometry, flow rate and electrolyte concentration. For a swirl flow, the correlations can be written as [26]:

$$Sh = k_L d / D = a Re^{2/3} Sc^{1/3} \quad (6)$$

where, Sh is the Sherwood number ($k_L d / D$), which is a dimensionless mass-transfer rate, Re is the Reynolds number ($d \rho U_m / \mu$) indicating dimensionless hydrodynamic conditions, Sc is the Schmidt number ($\mu / \rho D$), a is a constant that depends on the geometry, μ is the fluid viscosity and ρ is the fluid density. Since the electrical migration effects are negligible, due to the presence of a large excess of supporting electrolyte, and due to the limiting rate of deposition, the metal concentration is reduced to virtually zero at the electrode surface; the mass-transfer coefficient k_L due to diffusion and convection can be related to the limiting current density (i_L , A cm^{-2}), by the following equation:

$$k_L = i_L / (z F A C_b) \quad (7)$$

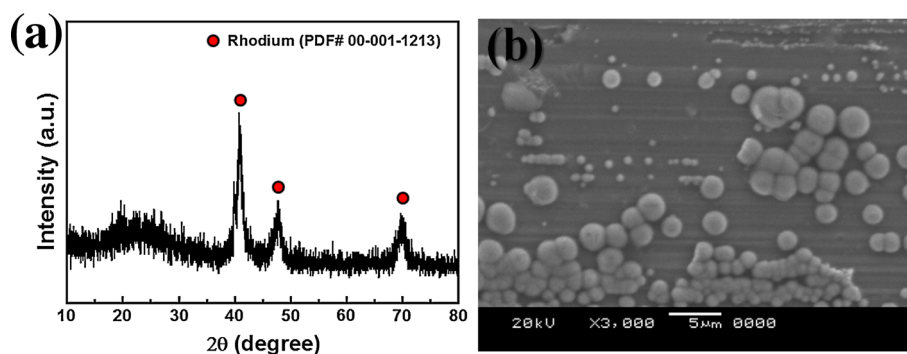
where, z is the number of electrons involved in the electrode reaction, F is the Faraday constant, A is the electrode surface area (cm^2) and C_b is the bulk concentration (mole cm^{-3}). For Reynolds number above 6,000, Sa et al. [27] suggested that the average Sherwood number would be as follows:

$$Sh = 0.091 Re^{0.8} Sc^{1/3} \quad (8)$$

The Sherwood number in terms of the Reynolds number, using Eqs. (4) and (5) for Rh deposition in the modified electrochemical cyclone cell, is presented in Fig. 7. The figure shows a good linear relation between Sh and Re , with a slope of 0.83, and agrees well with the results for Cu [26], Pd [18] and Pt [19].

Figure 8 shows XRD data and the morphology of rhodium deposited from the low rhodium concentration. The peaks in Fig. 8a were identified as rhodium phase (PDF# 00-001-1213). In Fig. 8b, nodular-type agglomerates of a few microns in size were deposited on the cathode surface, which is a typical phenomenon, under limited mass-transfer conditions.

Fig. 8 XRD data and SEM morphology of rhodium deposited from the low concentration



4 Conclusions

The electrochemical behaviour of rhodium was investigated using a rotating disc electrode, and the electrowinning of rhodium was performed by a modified cyclone cell in an acidic chloride solution. As the potential decreased, the reduction reaction of Rh^{3+} seemed to occur sequentially to form Rh^{2+} , Rh^+ and the metallic rhodium. The diffusion coefficient and activation energy were obtained from rotating disc electrode experiments as $6.3 \times 10^{-6} \text{ cm}^2 \text{ s}^{-1}$ and $11.14 \text{ kJ mol}^{-1}$, respectively. The optimum applied voltage of the cyclone cell was determined to be 3 V, considering the energy consumption. Under the optimal conditions, more than 91 % of the rhodium metal could be recovered in an acidic solution within 2 h. The electrowinning of rhodium using the modified electrochemical cyclone reactor is a potential process for efficiently recovering precious metal from dilute solutions.

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